MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

Quarterly Technical Report

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ABSTRACT

This quarterly report summarizes the efforts and accomplishments related to investigations of releases of mercury and other air toxic elements from coal combustion by-products (CCBs). This report focuses on laboratory efforts related to characterization of CCBs and leaching and ambient- and elevated-temperature release experiments. Data are presented for a variety of samples evaluated. Field data and samples collected in a previous quarter are also discussed and preliminary results presented. Initial data reduction and interpretation efforts for leaching data are presented including preliminary observations. A summary of technology transfer efforts accomplished and plans for the next quarter are also included.

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LIST OF ACRONYMS

CAARC	Coal Ash Resources Research Consortium
CCB	coal combustion by-product
DMA	digital mercury analyzer
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
FGD	flue gas desulfurization
LOI	loss on ignition
LTL	long-term leaching
NETL	National Energy Technology Laboratory
SDA	spray dryer absorber
SGLP	synthetic groundwater leaching procedure
SPME	solid-phase microextraction
TCLP	toxicity characteristic leaching procedure
UNR	University of Nevada – Reno

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EXECUTIVE SUMMARY

During the first quarter of 2005, this project focused on continued laboratory evaluations including the assessment of mercury releases from coal combustion by-products (CCBs) exposed to elevated temperatures. This was coupled with evaluation of the total mercury concentration of samples that had been exposed to a temperature of 750°C with results indicating that nearly all samples showed no measurable mercury remaining. Ambient temperature release experiments were also in progress during the quarter, and measurements of mercury releases were made after 90 days of exposure to low-mercury air. The first sample of wet flue gas desulfurization (FGD) material tested in this project required a modification to the ambient temperature desorption experimental setup, and it released higher levels of mercury than fly ash samples measured previously. The ambient temperature release experiments will continue into the next quarter.

Field data was assembled, and preliminary assessments of the data were made. The field flux measurements indicated that low-level releases of mercury similar to background releases occurred at most of the locations at the disposal sites evaluated.

Preliminary leaching data reduction was performed using data assembled during the first 2 years of the project. Comparisons of total mercury concentrations of CCB samples generated both from systems with and without mercury controls present with leachate concentrations continued to support the observation that total mercury concentration does not correlate with leachate concentrations of mercury. For some air toxic elements, similarities among samples by coal type (bituminous, subbituminous, and ligntite) in total concentrations and associated leachate concentrations were noted, but data was insufficient to determine if this was a trend. In samples containing activated carbon, the leachate concentrations of some air toxic elements were lower than samples without activated carbon, potentially indicating that leached elements may be sorbed by the activated carbon.

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INTRODUCTION

This effort is focused on the evaluation of coal combustion by-products (CCBs) for their potential to release mercury and other air toxic elements under different controlled laboratory conditions and will investigate the release of these same air toxic elements in select disposal and utilization field settings to understand the impact of various emission control technologies. Information will be collected, evaluated, and interpreted together with past Energy & Environmental Research Center (EERC) data and similar data from other studies. Results will be used to determine if mercury release from CCBs, both as currently produced and as produced with mercury and other emission controls in place, will potentially impact CCB management practices. The project will provide data on the environmental acceptability of CCBs expected to be produced in systems with emission controls for typical disposal and utilization scenarios. The project will develop baseline information on release mechanisms of select elements in both conventional and modified or experimental CCBs. The modified or experimental CCBs will represent those from systems that have improved emission controls. Controlling these emissions has a high potential to change the chemical characteristics and environmental performance of CCBs. Development of reliable methods to determine the release of mercury from CCBs will provide a means of evaluating the environmental risk associated with CCB management practices. Using appropriate methods to develop data about currently produced CCBs and those produced under experimental or simulated conditions will provide a baseline for the CCB industry to understand the impact of various emission control technologies.

EXPERIMENTAL

Literature Search

Researchers continued to collect publications related to mercury, air toxic elements, and CCBs. Citations and abstracts were assembled and added to the Mercury and Air Toxic Element document database located at www.undeerc.org/carrc/mercury. This database is password-protected and only available to project researchers and sponsors.

Analytical Methods Selection

The original work proposed under the analytical method selection task was completed by preparation of a report summarizing the analytical and release methods selected for this project. As noted previously, the original scope of the task was expanded to include participation in a U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) informal interlaboratory comparative study of leaching procedures commonly applied to CCBs. During the last quarter, work on this subtask included leaching and associated analysis of leachates. Information was also provided to the NETL contact, Mr. Pete Hesbach, on the synthetic

groundwater leaching procedure (SGLP)–long-term leaching (LTL) for inclusion in a poster to be presented at the World of Coal Ash Conference.

Sample Identification and Selection

Sample prioritization, identification, and selection continued by making requests for samples from project sponsors, DOE NETL contractors involved in mercury emission testing, and EERC research staff. A critical review of the sample set was made, and preparation of a draft report on this task was initiated.

Chemical and Physical Characterization

Sixteen samples were analyzed for total mercury content. Distilled water pH values of six CCBs were determined. Moisture content and loss on ignition (LOI) were determined on 23 samples, including 11 that were collected in September 2004 under the Field Investigation task.

Laboratory Evaluation of Air Toxic Element Release

Leaching

The leaching subtask focused on performing leaching on one sample from the DOE NETL interlaboratory comparative leaching study. Leaching data from earlier work were evaluated under the data reduction task.

Vapor Transport

The second batch of long-term ambient-temperature mercury release experiments continued. Mercury release for the first 90-day period was evaluated. Sample 03-082 had shown a large release for the 7-day period reported last quarter. Therefore, it was decided to test this sample every 45 days instead of every 90 days as with the other samples. The second 90-day period collection was initiated. The third sample set blanking process continued.

Mercury thermal desorption curves were generated for numerous samples. The desorbed samples from 44 runs last quarter were analyzed for total remaining mercury using a digital mercury analyzer (DMA-80).

Microbiological Release

The blanking process continued for the microbiological release subtask.

Field Investigation

Chemical characterization of solid samples obtained in September was initiated. This included determination of total mercury content, pH, moisture content, and LOI.

Data Reduction and Interpretation

Data reduction focused on the leachate data generated over the first 2 years of this project. The data set was separated into two subsets: 1) samples from systems without mercury controls and 2) samples from systems with mercury controls. Only one sample pair, containing a pre- (a true baseline) and post-mercury control sample exists in the sample set, and since there is only this single paired set at this time, it was grouped with the other samples. Total mercury and air toxic element concentrations were compared with leachate concentrations in preliminary interpretive efforts. A comparison of SGLP and toxicity characteristic leaching procedure (TCLP) results was also made.

University of Nevada – Reno (UNR) completed data reduction from field investigations performed in fall 2004, and a revised final report was submitted. EERC field data were assembled into tables for further review and compared with UNR data.

Technology Transfer

Three presentations, "A Method for Determining Microbiologically Mediated Release of Elemental and Organomercury Compounds from CCBs Using SPME, Gas Chromatography, and Atomic Fluorescence," "Long-Term Storage of Air-Sampled Mercury on Gold-Coated Quartz Tubes," and "Real-Time Thermal Devolatilization of Mercury and Mercury Compounds from CCBs Detected with Atomic Absorption Spectrometry," were made at PITTCON® 2005, February 27–March 4, 2005, in Orlando, Florida.

Two papers were prepared for submission to the World of Coal Ash, and a paper was also prepared for submission to *Fuel*.

Preparations for the Year 2 Project Annual Meeting to be held in April 2005 were initiated and the draft Year 2 Annual Report was prepared for submission to project sponsors. Previously published project data were summarized at the Coal Ash Resources Research Consortium (CARRC) annual meeting February 17–18, 2005. Attendees at that meeting included representatives of the Minnesota Pollution Control Agency.

RESULTS AND DISCUSSION

Literature Search

This quarter, four documents were added to the Mercury and Air Toxic Element database, which now contains 419 documents.

Analytical Methods Selection

The key result of this task, as originally proposed, was a report of the analytical and release methods selected and developed to assess mercury and air toxic element release from CCBs for

this project. Comparative leaching study samples were leached and leachtes analyzed, and results from other cooperating laboratories were received.

Sample Identification and Selection

Five samples were added to the sample set. These included baseline and mercury control demonstration fly ash and flue gas desulfurization (FGD) material samples (including a spray dryer absorber [SDA] ash) from current demonstration projects.

Chemical and Physical Characterization

Total mercury concentrations as determined by using a DMA-80 are shown in Table 1. Table 2 shows the pH values for six CCB samples obtained using distilled water.

Table 1. Total Mercury Concentration, µg/g

ID No.	Sample Type	Mercury Control	Hg
03-065	Gypsum	No	0.044
03-067	FGD slurry	No	<0.1
03-089	FGD	No	0.096
04-055	Fly ash field sample	No	0.007
04-056	Wet FGD/pyrites field sample	No	0.187
04-057	Wet FGD/pyrites field sample	No	0.207
04-058	Soil field sample	No	0.05
04-059	Bottom ash field sample	No	0.044
04-060	Wet FGD field sample	No	0.299
04-061	Bottom ash field sample	No	0.001
04-062	Bottom ash field sample	No	<0.003
04-063	FGD/fly ash field sample	No	0.08
04-064	FGD/fly ash field sample	No	0.25
04-065	FGD/fly ash field sample	No	0.011
04-082	Gypsum	No	0.043
04-083	Gypsum	No	0.103

Table 2. CCB pH Values

ID No.	Sample Type	Mercury Control	pH
04-082	Gypsum	No	8.10
04-083	Gypsum	No	8.10
05-001	Fly ash	No	12.84
05-002	FGD–SDA	No	12.85
05-003	Fly ash	Yes	12.85
05-004	FGD–SDA hopper ash	Yes	13.06

Table 3 shows the moisture content and LOI for 23 samples analyzed this quarter. This included 11 samples collected under the Field Investigation task in September 2004.

Table 3. Moisture Content and LOI, %

ID No.	Sample Type	Mercury Control	Moisture Content	LOI
03-004	Fly ash	No	0.15	3.20
03-007	Fly ash	No	0.19	4.41
04-007	Fly ash	No	0.05	2.46
04-031	Fly ash	Yes	0.12	0.64
04-032	Fly ash	Yes	0.11	1.09
04-035	Fly ash	No	0.06	2.24
04-055	Fly ash field sample	No	14.8	5.73
04-056	Wet FGD/pyrites field sample	No	21.3	3.31
04-057	Wet FGD/pyrites field sample	No	19.3	2.18
04-058	Soil field sample	No	12.6	6.88
04-059	Bottom ash field sample	No	7.02	1.99
04-060	Wet FGD field sample	No	23.3	2.49
04-061	Bottom ash field sample	No	16.2	13.0
04-062	Bottom ash field sample	No	28.8	7.73
04-063	FGD/fly ash field sample	No	15.0	3.40
04-064	FGD/fly ash field sample	No	23.5	2.68
04-065	FGD/fly ash field sample	No	10.1	3.68
04-082	Gypsum	No	26.6	1.60
04-083	Gypsum	No	26.6	2.26
05-001	Fly ash	No	1.00	0.90
05-002	FGD–SDA hopper ash	No	1.08	0.95
05-003	Fly ash	Yes	0.85	1.04
05-004	FGD–SDA hopper ash	Yes	0.75	1.12

Laboratory Evaluation of Air Toxic Element Release

Leaching

Results were received for SGLP and 30- and 60-day LTL leachates. The results of all leaching tests are shown in Table 4. Leaching data from other cooperating laboratories in the DOE NETL comparative leaching study were received and reviewed.

Vapor Transport

Results of the first 90-day period of release in the long-term ambient-temperature mercury release experiment are shown in Table 5. The first two 45-day periods of release for Sample 03-082 are shown in Table 6.

Table 4. Trace Element Leachate Concentrations, µg/L

ID No.	Test	Sample Type	Mercury Control	As	Cd	Cr	Pb	Ni	Se	pH
04-034	SGLP	Fly ash	No	30	0.22	29	<1.0	5.8	110	12.18
04-034	SGLP	Fly ash	No	31	0.20	30	<1.0	6.1	110	12.20
04-034	SGLP	Fly ash	No	31	0.23	30	<1.0	6.0	110	12.20
04-034	30-day LTL	Fly ash	No	16	0.28	63	<1.0	3.9	14	11.89
04-034	30-day LTL	Fly ash	No	15	0.26	62	<1.0	4.0	13	11.89
04-034	30-day LTL	Fly ash	No	15	0.27	63	<1.0	4.3	12	11.92
04-034	60-day LTL	Fly ash	No	16	0.48	80	<1.0	<2.0	18	11.68
04-034	60-day LTL	Fly ash	No	16	0.50	90	<1.0	<2.0	23	11.68
04-034	60-day LTL	Fly ash	No	16	0.52	80	<1.0	<2.0	22	11.71

Table 5. Ambient-Temperature Mercury Release in First 90-Day Period, pg/g/day

ID No.	Sample Type	Mercury Control	Bottle 1	Bottle 2
Blank	Fired quartz sand	No	0.00024	0.00013
04-006	Fly ash	No	<0.00001	0.00003
04-007	Fly ash	No	0.00005	0.00006
04-035	Fly ash	No	0.00004	0.00006
04-036	Fly ash	Yes	0.00004	0.00005
04-054	Fly ash	Yes	0.00003	0.00008
04-067	Fly ash	Yes	0.00004	<0.00001

Table 6. Ambient-Temperature Mercury Release in First Two 45-Day Periods for Sample 03-082, pg/g/day

ID No.	Sample Type	Mercury Control	45-Day Period	Bottle 1	Bottle 2
03-082	FGD filtercake	No	First	1.784	0.2896
03-082	FGD filtercake	No	Second	1.385	0.3289

Mercury thermal desorption curves were generated for the six samples listed in Table 7. Replicate runs were performed on a few of the samples. Replicate runs will be interpreted when replicates on more samples have been completed. The spent samples from 44 runs last quarter were analyzed for total remaining mercury using a DMA-80. All but two spent samples showed no measurable mercury remaining. Triplicate evaluations of thermal release were performed on one fly ash sample with activated carbon (04-054), and DMA-80 results on all three desorbed samples showed mercury remaining.

Microbiological Release

There are no results for this quarter.

Table 7. CCB Samples Tested for Mercury Thermal Desorption

ID No.	Sample Type	Mercury Control	# Runs
03-018	Fly ash	Yes	2
04-035	Fly ash	No	2
04-036	Fly ash	Yes	2
04-054	Fly ash	Yes	3
04-067	Fly ash	Yes	2
05-001	Fly ash	No	1

Field Investigation

Results of chemical characterization activities on field samples are included in previous sections of this report (see Tables 1–3). UNR concluded that the results of the field sampling indicated that there may be a very limited outward flux of mercury at the facilities tested.

Data Reduction and Interpretation

As already noted, the samples collected to date for this project were separated into two subsets: 1) samples from systems without mercury controls and 2) samples from systems with mercury controls. Total mercury and air toxic element concentrations were compared with leachate concentrations in preliminary interpretive efforts. A comparison of SGLP and TCLP results was also made. The comparison of total mercury concentrations for CCBs with the leachate concentrations supported the preliminary conclusion that the leachable mercury does not correlate with total mercury concentrations. Other observations include the following:

1) For some air toxic elements, there may be similarities among samples from coal types (bituminous, subbituminous, and ligntite) in total concentrations and associated leachate concentrations as noted by groupings within some of the graphs comparing total and leaching concentrations. For some coal types, only a very limited number of samples were evaluated, so the observation will be assessed as additional data is generated over the duration of the project.

2) The leachate concentrations of some air toxic elements were lower in samples containing activated carbon than in samples without activated carbon. One proposed explanation may be that leached elements may be sorbed by the activated carbon. This phenomenon will be evaluated in continuing data reduction and interpretation efforts.

PLANS FOR NEXT QUARTER

During the next quarter, laboratory activities will continue. Characterization of samples will continue with moisture, LOI, total mercury, and confirmation of carbon forms. Laboratory experiments will also include the leaching for the DOE NETL informal interlaboratory comparison on leaching procedures, standard leaching on new samples as received, ambient-

temperature vapor-phase release experiments, and microbiologically mediated mercury release experiments. Analytical activities on samples generated from the release experiments will continue as samples are generated.

Review of the UNR field investigation report will continue, and EERC and UNR researchers expect to collaborate to evaluate and interpret the EERC and UNR field data.

The topical report on sample identification and collection will be completed and submitted to project sponsors. Preliminary plans will be made for potential field evaluations for Year 3 of the project. A topical report of leaching data will be assembled and submitted to project sponsors. Preparation of a presentation for the DOE NETL Mercury Control Technology R&D Program Review scheduled for July 12–14, 2005, will be initiated.

The Year 2 Annual Meeting will be held in Lexington, Kentucky, April 12, 2005, in conjunction with the World of Coal Ash Conference. A Year 2 draft final report will be distributed to project sponsors at the meeting.